

## Structure of 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3- $\mu$ -methoxymethylidene-2,3- $\mu$ -triphenylphosphineaurio-triangulo-triosmium

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**Abstract.**  $[\text{AuOs}_3(\mu\text{-COCH}_3)(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ ,  $M_r = 1353.0$ , triclinic,  $P\bar{1}$ ,  $a = 12.940(4)$ ,  $b = 15.680(9)$ ,  $c = 17.462(4)$  Å,  $\alpha = 107.70(3)$ ,  $\beta = 95.39(3)$ ,  $\gamma = 90.67(4)^\circ$ ,  $V = 3358(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.67$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 136.15$  cm<sup>-1</sup>,  $F(000) = 2432$ ,  $T = 298$  K,  $R = 0.032$  for 9126 observed reflections. The two gold–triosmium clusters in the asymmetric unit are closely similar and related by rotation of the  $\text{PPh}_3$  and  $\text{COCH}_3$  ligands. The angle between the  $\text{Os}_3$  and  $\text{Os}(\mu\text{-C})\text{Os}$  planes is  $103.8(5)$  [ $102.9(5)^\circ$ ] with the  $\text{Os}\cdots\text{C}(\text{alkylidene})$  contact distances  $3.11(1)$  [ $3.097(9)$  Å]. The methoxymethylidene moiety is thus best described as a  $\mu_2$  ligand.

**Introduction.** There is recent interest in semi-bridging interactions involving the  $\mu$ -alkylidene ligand and the 18-electron, coordinatively saturated,  $\text{Os}(\text{CO})_4$  unit in clusters of the type  $[\text{Os}_3(\mu\text{-H})(\mu\text{-CR})(\text{CO})_{10}]$  (Shapley, Cree-Uchiyama, St George, Churchill & Bueno, 1983; Yeh, Shapley, Li & Churchill, 1985; Green, Orpen & Shaverien, 1984). Similar interactions involving the Co atom in  $[\text{CoFe}_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$  have also been described (Aitchison & Farrugia, 1986). The title complex (1), prepared by reaction of  $\text{AuCH}_3(\text{PPh}_3)$  with  $[\text{Os}_3(\mu\text{-H})(\mu\text{-COCH}_3)(\text{CO})_{10}]$  in toluene at 363 K was examined crystallographically to provide further information concerning the steric and electronic effects on the  $\mu$ -alkylidene bonding mode caused by substitution of a  $\mu\text{-H}$  group by the isolobal  $\mu\text{-AuPPh}_3$  unit. The isostructural ruthenium analogue of (1) has been structurally examined (Bateman, Green, Mead, Mills, Salter, Stone & Woodward, 1983) but poorly determined owing to crystal decomposition.

**Experimental.** Orange-yellow prisms from dichloromethane–hexane solution: crystal dimensions  $0.2 \times 0.4 \times 0.3$  mm; systematic absences: none; Enraf–Nonius CAD-4F diffractometer; graphite monochromator;  $\theta/2\theta$  scan mode; cell parameters refined by least-squares methods on basis of 25 independent  $\theta$  values,  $8 < \theta < 13^\circ$ ; intensities measured to  $\theta = 27.5^\circ$ ; range of  $hkl$  0 to 16,  $-22$  to  $+22$ ,  $-23$  to  $+23$ ; 157, 226, 108 measured every 2 h with 5% decay over 293 h of data collection; 16 685 reflections measured, 15 881 independent data with 9126 having  $I > 2.5\sigma(I)$

considered observed and used in structure determination and refinement;  $R_{\text{int}}$  before absorption correction 0.041, after correction 0.026; corrected for Lorentz, polarization and absorption (DIFABS; Walker & Stuart, 1983); solved by direct methods (MITHRIL; Gilmore, 1984) and subsequent block-diagonal and final blocked full-matrix least squares; anisotropic thermal parameters for all non-H atoms; H atoms included in fixed calculated positions,  $U_{\text{iso}} = 0.05$  Å<sup>2</sup>;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o)]^{-1}$ ; max.  $\Delta/\sigma$  0.174, av. 0.037;  $(\Delta\rho)_{\text{max}} + 1.15$ ,  $(\Delta\rho)_{\text{min}} - 2.44$  e Å<sup>-3</sup> in proximity of heavy atoms;  $R = 0.032$ ,  $wR = 0.038$ ;  $R(wR) = 0.093$  (0.042) for all data;  $S = 1.55$ ; atomic scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974); calculations carried out on a Gould-SEL 32/27 minicomputer using the GX suite of programs (Mallinson & Muir, 1985).

**Discussion.** Final positional parameters for non-H atoms are given in Table 1, with selected bond distances and angles in Table 2.\* The two independent molecules in the asymmetric unit, shown in Figs. 1 and 2, are related by a minor configurational twist of the  $\text{PPh}_3$  ligand and a  $180^\circ$  rotation of the  $\text{COCH}_3$  group about the C(11)–O(11) bond. Stereochemically equivalent atoms in the two cluster units are labelled correspondingly. Bond-length and -angle differences between the molecules are generally marginal, though some metal–metal separations, particularly Os(1)–Au(1), show significant ( $17\sigma$ ) deviations. The strong *trans* effect of the  $\text{COCH}_3$  ligand is visible in longer Os(1)–C(2), Os(2)–C(6) vectors *trans* to this ligand, compared with those carbonyls *trans* to metal–metal bonds (Table 2). The C(11)–O(11) distance implies substantial  $\pi$  character for this bond.

\* Lists of structure factors, anisotropic thermal parameters for all non-H atoms, calculated positional parameters for H atoms, a complete listing of bond lengths and angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42756 (96 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters (fractional coordinates) with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters,  $U_{eq}(\text{\AA}^2)$

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Molecule (I)	x	y	z	$U_{eq}$
Os(1)	0.37017 (3)	0.40167 (3)	0.72597 (3)	0.037
Os(2)	0.24032 (4)	0.54589 (3)	0.71385 (3)	0.039
Os(3)	0.38651 (4)	0.56984 (3)	0.85254 (3)	0.039
Au(1)	0.15392 (4)	0.38125 (3)	0.70687 (3)	0.042
P(1)	0.0097 (2)	0.2881 (2)	0.6952 (2)	0.046
C(1)	0.5136 (8)	0.3931 (7)	0.7467 (7)	0.043
C(2)	0.3320 (9)	0.3409 (7)	0.8026 (8)	0.054
C(3)	0.3524 (9)	0.2980 (8)	0.6326 (7)	0.052
C(4)	0.1488 (11)	0.5214 (8)	0.6181 (8)	0.065
C(5)	0.2732 (11)	0.6628 (8)	0.7153 (9)	0.077
C(6)	0.1331 (10)	0.5790 (9)	0.7893 (8)	0.069
C(7)	0.2842 (9)	0.5139 (8)	0.8974 (7)	0.047
C(8)	0.4821 (10)	0.6161 (8)	0.7952 (7)	0.058
C(9)	0.4984 (11)	0.5500 (10)	0.9234 (9)	0.077
C(10)	0.3438 (12)	0.6821 (8)	0.9135 (8)	0.070
C(11)	0.3666 (9)	0.4917 (8)	0.6648 (6)	0.048
C(12)	0.5140 (12)	0.4636 (13)	0.5918 (10)	0.104
C(111)	0.0314 (10)	0.1679 (8)	0.6555 (7)	0.057
C(112)	0.1029 (10)	0.1425 (8)	0.5983 (7)	0.054
C(113)	0.1225 (10)	0.0513 (10)	0.5682 (8)	0.062
C(114)	0.0754 (12)	-0.0087 (9)	0.5954 (8)	0.068
C(115)	0.0082 (12)	0.0176 (10)	0.6516 (9)	0.078
C(116)	-0.0112 (11)	0.1082 (9)	0.6838 (8)	0.069
C(121)	-0.0973 (8)	0.3072 (8)	0.6285 (7)	0.048
C(122)	-0.1136 (10)	0.3943 (9)	0.6288 (9)	0.070
C(123)	-0.1911 (11)	0.4144 (11)	0.5783 (9)	0.078
C(124)	-0.2530 (11)	0.3419 (13)	0.5248 (8)	0.077
C(125)	-0.2356 (10)	0.2577 (11)	0.5236 (9)	0.073
C(126)	-0.1603 (10)	0.2370 (9)	0.5748 (9)	0.067
C(131)	-0.0429 (10)	0.3036 (8)	0.7902 (7)	0.054
C(132)	-0.1477 (10)	0.3162 (8)	0.8000 (8)	0.054
C(133)	-0.1801 (12)	0.3296 (9)	0.8761 (9)	0.071
C(134)	-0.1117 (13)	0.3278 (11)	0.9388 (9)	0.079
C(135)	-0.0094 (13)	0.3132 (15)	0.9309 (9)	0.111
C(136)	0.0271 (11)	0.3056 (14)	0.8568 (10)	0.100
O(1)	0.6018 (6)	0.3897 (6)	0.7629 (6)	0.078
O(2)	0.3103 (7)	0.3036 (6)	0.8466 (6)	0.074
O(3)	0.3480 (8)	0.2371 (6)	0.5768 (6)	0.084
O(4)	0.0930 (8)	0.5154 (7)	0.5632 (6)	0.098
O(5)	0.2947 (10)	0.7327 (6)	0.7128 (8)	0.121
O(6)	0.0733 (7)	0.6024 (7)	0.8345 (6)	0.094
O(7)	0.2250 (7)	0.4861 (6)	0.9278 (5)	0.067
O(8)	0.5389 (7)	0.6438 (7)	0.7608 (6)	0.084
O(9)	0.5687 (7)	0.5412 (10)	0.9646 (7)	0.134
O(10)	0.3066 (9)	0.7470 (6)	0.9486 (7)	0.108
O(11)	0.4225 (7)	0.5123 (6)	0.6147 (5)	0.073

Molecule (II)	x	y	z	$U_{eq}$
Os(1')	0.49641 (3)	0.01218 (3)	0.16649 (3)	0.032
Os(2')	0.47488 (3)	0.06659 (3)	0.33680 (3)	0.033
Os(3')	0.46312 (4)	-0.11991 (3)	0.24502 (3)	0.043
Au(1')	0.33229 (3)	0.11292 (3)	0.22992 (3)	0.035
P(1')	0.1836 (2)	0.1876 (2)	0.2153 (2)	0.037
C(1')	0.5845 (10)	-0.0620 (8)	0.0990 (7)	0.053
C(2')	0.3700 (9)	-0.0355 (7)	0.0914 (7)	0.049
C(3')	0.5167 (9)	0.1134 (7)	0.1314 (6)	0.048
C(4')	0.4875 (8)	0.1921 (8)	0.3825 (7)	0.049
C(5')	0.5556 (9)	0.0406 (7)	0.4216 (7)	0.053
C(6')	0.3385 (9)	0.0536 (8)	0.3756 (7)	0.053
C(7')	0.3156 (10)	-0.1071 (7)	0.2257 (8)	0.056
C(8')	0.6122 (9)	-0.1193 (7)	0.2656 (7)	0.046
C(9')	0.4609 (9)	-0.2251 (8)	0.1520 (7)	0.053
C(10')	0.4383 (11)	-0.1683 (9)	0.3290 (9)	0.071
C(11')	0.5918 (7)	0.0559 (7)	0.2699 (6)	0.036
C(12')	0.7637 (9)	0.0622 (10)	0.2341 (8)	0.066
C(111')	0.2018 (8)	0.2777 (7)	0.1713 (6)	0.039
C(112')	0.1737 (10)	0.3643 (8)	0.2077 (8)	0.066
C(113')	0.1854 (12)	0.4294 (9)	0.1719 (11)	0.082
C(114')	0.2264 (13)	0.4088 (11)	0.0991 (10)	0.088
C(115')	0.2537 (12)	0.3232 (11)	0.0629 (8)	0.074
C(116')	0.2435 (11)	0.2592 (9)	0.1007 (7)	0.064
C(121')	0.1345 (10)	0.2383 (8)	0.3127 (7)	0.052
C(122')	0.0296 (11)	0.2332 (9)	0.3228 (9)	0.069
C(123')	-0.0027 (15)	0.2707 (11)	0.3981 (14)	0.104
C(124')	0.067 (2)	0.307 (1)	0.463 (1)	0.106
C(125')	0.1699 (18)	0.3140 (13)	0.4542 (9)	0.107
C(126')	0.2052 (11)	0.2774 (10)	0.3768 (8)	0.073
C(131')	0.0737 (8)	0.1198 (7)	0.1540 (6)	0.041
C(132')	-0.0016 (9)	0.1569 (8)	0.1120 (8)	0.056
C(133')	-0.0860 (11)	0.1051 (11)	0.0719 (9)	0.071

Table 1 (cont.)

	x	y	z	$U_{eq}$
C(134')	-0.0991 (11)	0.0187 (11)	0.0698 (8)	0.071
C(135')	-0.0267 (11)	-0.0179 (9)	0.1105 (9)	0.069
C(136')	0.0602 (10)	0.0329 (8)	0.1519 (7)	0.053
O(1')	0.6413 (8)	-0.1077 (8)	0.0592 (6)	0.097
O(2')	0.3040 (7)	-0.0640 (7)	0.0467 (6)	0.085
O(3')	0.5248 (8)	0.1717 (6)	0.1080 (6)	0.089
O(4')	0.4988 (8)	0.2673 (5)	0.4125 (6)	0.085
O(5')	0.6082 (8)	0.0244 (7)	0.4715 (5)	0.089
O(6')	0.2611 (7)	0.0441 (8)	0.3978 (6)	0.100
O(7')	0.2297 (7)	-0.1007 (6)	0.2122 (7)	0.099
O(8')	0.7001 (7)	-0.1203 (6)	0.2790 (6)	0.075
O(9')	0.4552 (8)	-0.2862 (6)	0.0982 (6)	0.087
O(10')	0.4242 (8)	-0.1953 (7)	0.3800 (6)	0.095
O(11')	0.6888 (5)	0.0754 (5)	0.2912 (5)	0.051

Table 2. Selected bond lengths (Å) and bond angles (°) for molecule (I); figures in square brackets refer to correspondingly labelled values for molecule (II)

Os(1)—Os(2)	2.880 (1)	[2.875 (1)]	Os(1)—C(11)	2.01 (1)	[2.02 (1)]
Os(1)—Os(3)	2.870 (1)	[2.859 (1)]	Os(2)—C(11)	2.00 (1)	[1.98 (1)]
Os(2)—Os(3)	2.856 (1)	[2.870 (1)]	Os(3)—C(7)	1.93 (1)	[1.93 (1)]
Os(1)—Au(1)	2.790 (1)	[2.773 (1)]	Os(3)—C(8)	1.93 (1)	[1.93 (1)]
Os(2)—Au(1)	2.765 (1)	[2.761 (1)]	Os(3)—C(9)	1.91 (2)	[1.93 (1)]
Os(1)—C(1)	1.87 (1)	[1.87 (1)]	Os(3)—C(10)	1.88 (1)	[1.89 (1)]
Os(1)—C(2)	1.96 (1)	[1.98 (1)]	C(11)—O(11)	1.30 (2)	[1.28 (1)]
Os(1)—C(3)	1.91 (1)	[1.89 (1)]	O(11)—C(12)	1.44 (2)	[1.43 (2)]
Os(2)—C(4)	1.89 (1)	[1.88 (1)]	Au(1)—P(1)	2.311 (3)	[2.298 (3)]
Os(2)—C(5)	1.87 (1)	[1.88 (1)]	Os(3)...C(11)	3.11 (1)	[3.097 (9)]
Os(2)—C(6)	1.97 (1)	[1.98 (1)]	Os(1)...C(7)	3.28 (1)	[3.40 (1)]
			Os(2)...C(7)	3.39 (1)	[3.37 (1)]

C(11)—O(11)—C(12) 119.6 (12) [122.5 (9)]

Os(1)—C(11)—Os(2) 92.0 (5) [92.2 (4)]

Os—C—O (carbonyl) range 179.7 (11)—172.5 (10) [178.5 (13)—175.9 (11)]

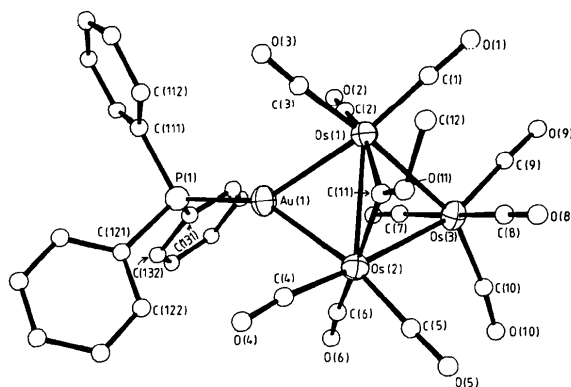


Fig. 1. The molecular structure of complex (1) (molecule I).

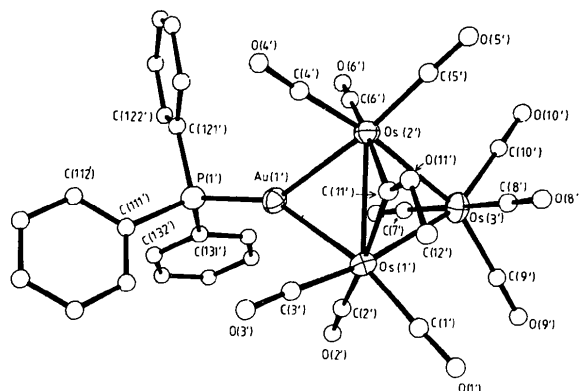


Fig. 2. The molecular structure of complex (1) (molecule II).

The angle between the plane Os(1)–C(11)–Os(2) and the triosmium plane of 103.8 (5)° [102.9 (5)° for molecule II] together with the Os(3)···C(11) contact distance of 3.11 (1) Å [3.097 (9) Å] indicates minimal semi- $\mu_3$  character of the alkylidyne ligand, *cf.* corresponding values for [Os<sub>3</sub>( $\mu$ -H)( $\mu_3$ -CPh)(CO)<sub>10</sub>] of 78.2° and 2.586 (10) Å (Yeh *et al.*, 1985) and [Os<sub>3</sub>( $\mu$ -H)( $\mu_3$ -CCH<sub>2</sub>CHMe<sub>2</sub>)(CO)<sub>10</sub>] of 82.1° and 2.640 (26) Å (Green *et al.*, 1984). Although [Os<sub>3</sub>( $\mu$ -H)( $\mu$ -COCH<sub>3</sub>)(CO)<sub>10</sub>] is structurally undetermined, the related complex [Os<sub>3</sub>( $\mu$ -H)( $\mu$ -CN(H)Bu<sup>t</sup>)(CO)<sub>10</sub>] (Adams & Golembeski, 1979), also with a  $\pi$ -donor substituent, has a much greater corresponding interplanar angle of 106°, implying a markedly weaker interaction. These data taken together suggest only a minimal increase in alkylidyne  $\mu_3$  character in complex (1) on substitution of  $\mu$ -H by  $\mu$ -AuPPh<sub>3</sub>, in contrast to previous observations for [CoFe<sub>2</sub>( $\mu$ -H)( $\mu_3$ -COCH<sub>3</sub>)(CO)<sub>7</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>)] and the  $\mu$ -AuPPh<sub>3</sub> analogue (Aitchison & Farrugia, 1986). Moreover, in the [Ru<sub>3</sub>( $\mu$ -X)( $\mu$ -COCH<sub>3</sub>)(CO)<sub>10</sub>] system there is an *increase* in the interplanar angle in going from the hydrido (94.9°) (Churchill, Beanan, Wasserman, Bueno, Rahman & Keister, 1983) to the aurio derivative (av. 101°) (Bateman *et al.*, 1983). These results imply that steric rather than electronic factors are of principal importance in the configurational differences observed, in view of the lack of a consistent pattern.

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## Structures of 1,10-(1,1'-Ruthenocenediyl)-1,10-dioxo-4,7-dithiadecane (I) and its PdCl<sub>2</sub> Complex (II)

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**Abstract.** (I), C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>RuS<sub>2</sub>, *M<sub>r</sub>* = 409.6, monoclinic, *C*2/*c*, *a* = 27.393 (4), *b* = 11.966 (2), *c* = 10.375 (2) Å,  $\beta$  = 110.83 (1)°, *V* = 3178.3 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.71 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.7107 Å,  $\mu$  = 12 cm<sup>-1</sup>, *F*(000) = 1664, *T* = 297 K, *R* = 0.033 for 2248 observed reflections. (II), C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>RuS<sub>2</sub>.PdCl<sub>2</sub>, *M<sub>r</sub>* = 586.9, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 14.225 (4), *b* = 12.235 (3), *c* = 10.778 (3) Å, *V* = 1877.6 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.08 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.7107 Å,  $\mu$  = 22 cm<sup>-1</sup>, *F*(000) = 1152, *T* = 297 K, *R* = 0.055 for

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